PB85-239903

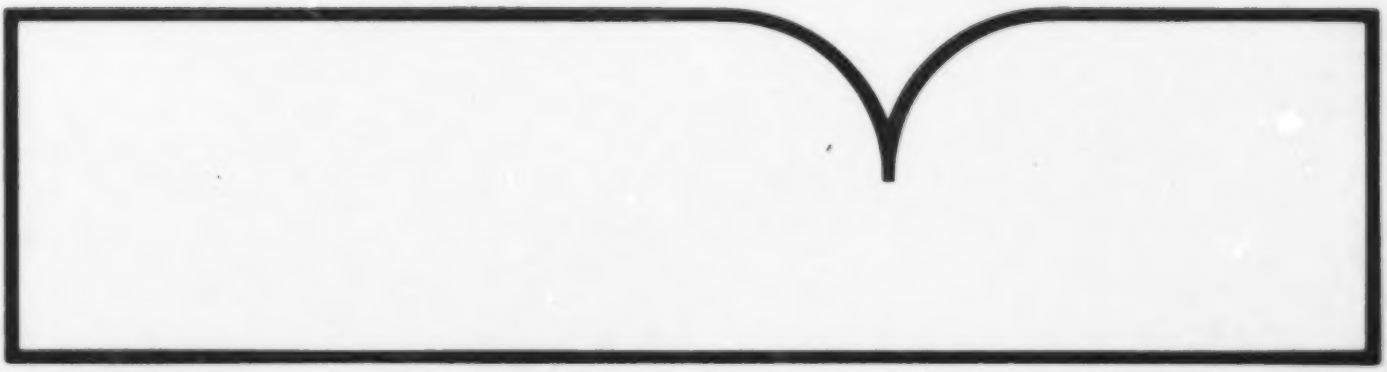
Chemical Weathering and Solution Chemistry in Acid Forest Soils Differential Influence of Soil Type, Biotic Processes, and H+ Deposition

Maine Univ. at Orono

Prepared for

Corvallis Environmental Research Lab., OR

Aug 85



U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/D-85/176	2.
3. RECIPIENT'S ACCESSION NO. PB85 239903/AS	
4. TITLE AND SUBTITLE Chemical Weathering and Solution Chemistry in Acid Forest Soils: Differential Influence of Soil Type, Biotic Processes, and H+ Deposition	5. REPORT DATE August 1985
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) C. S. Cronan	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Dept of Botany & Plant Pathology University of Maine Orono, ME 04469	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO. EPA/NCSU APP-0026M-1980
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Corvallis, OR 97333	13. TYPE OF REPORT AND PERIOD COVERED Extramural reprint
	14. SPONSORING AGENCY CODE EPA/600/02
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

In this investigation, weathering rates were calculated for three eastern North American forest soils using five separate estimation techniques. In addition, leaching experiments were performed to examine the influence of selected environmental variables on the weathering process. Weathering rates varied five-fold between soils, ranging from approximately 0.5 Keq ha^{-1} yr^{-1} in a sandy Adams Spodosol, to 1.2 Keq ha^{-1} yr^{-1} in a sandy loam Becket Spodosol, to 2.7 Keq ha^{-1} yr^{-1} in a silty Unadilla Inceptisol. Inter-soil differences in weathering rate were inversely correlated with mean soil particle size and positively correlated with total exchangeable bases in the soil profile. Study results also demonstrated major differences in weathering rates between soil horizons.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 25
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE $7.00

EPA Form 2220-1 (9-73)

PB85-239903

EPA/600/D-85/176
August 1985

Chemical Weathering and Solution Chemistry in Acid Forest Soils:

Differential Influence of Soil Type, Biotic Processes, and H^+ Deposition

by

Christopher S. Cronan
Department of Botany & Plant Pathology
University of Maine
Orono, ME 04469

NSCU/EPA Contract
APP0026-1980

EPA Project Officer
Raymond G. Wilhour

Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Corvallis, OR 97333

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

CHEMICAL WEATHERING AND SOLUTION CHEMISTRY IN ACID FOREST SOILS: DIFFERENTIAL INFLUENCE OF SOIL TYPE, BIOTIC PROCESSES, AND H^+ DEPOSITION

Christopher S. Cronan*

Department of Botany & Plant Pathology
University of Maine at Orono
Orono, Maine 04469

ABSTRACT

In this investigation, weathering rates were calculated for three eastern North American forest soils using five separate estimation techniques. In addition, leaching experiments were performed to examine the influence of selected environmental variables on the weathering process. Weathering rates varied five-fold between soils, ranging from approximately 0.5 Keq $ha^{-1} yr^{-1}$ in a sandy Adams Spodosol, to 1.2 Keq $ha^{-1} yr^{-1}$ in a sandy loam Becket Spodosol, to 2.7 Keq $ha^{-1} yr^{-1}$ in a silty Unadilla Inceptisol. Inter-soil differences in weathering rate were inversely correlated with mean soil particle size and positively correlated with total exchangeable bases in the soil profile. Study results also demonstrated major differences in weathering rates between soil horizons.

*Supported by NCSU/EPA Contract APP0026-1980.

INTRODUCTION

There are a number of compelling reasons for studying weathering processes in natural systems. From a geochemical perspective, weathering reactions are critical to the distribution and transport fate of a significant number of elements. Without improved understanding of weathering reaction thermodynamics, kinetics, and responses to environmental variation, it will be impossible to develop effective models for predicting the geochemical behavior of these elements. From an ecological perspective, there is an additional critical need to quantify the variable contribution of weathering to base supply (Ca + Mg + K + Na) in natural ecosystems. For example, base supply rate may determine long-term site quality in areas that are subjected to whole-tree harvesting of the forest resource. Likewise, base supply rate from primary weathering may control the fate of terrestrial and aquatic systems that are exposed to chronic acid deposition from the atmosphere.

The objective of this investigation was to estimate weathering rates for representative acid forest soils in northeastern North America and to examine the influence of selected environmental variables on the weathering process. This field and laboratory study was conducted using three forest soils from the northeastern U.S. Conceptually, the research was designed to address a framework of testable hypotheses. The primary null hypothesis for the investigation was as follows: there are no differences in weathering rates between separate acid forest soils in northeastern North America. Besides this general hypothesis, the investigation also considered the following kinds of more specific hypotheses.

* Weathering rate in the soil is inversely porportional to mean grain size and increases with surface area.

* Weathering is a rate-limited non-equilibrium process which increases per unit area with decreasing soil permeability and increasing water residence time.

* The weathering rate of base cations is proportional to the concentration of bases in the

primary mineral substrate.

* Weathering varies as a function of vegetative cover and its influence on dry deposition and uptake-coupled proton release.

* Weathering rate is controlled by the leachate chemistry of the biologically-derived forest floor. Weathering increases as a function of organic ligand concentrations and their influence on metal complexation and free metal activities.

* Weathering increases as a function of H^+ inputs from atmospheric deposition and internal generation by biota.

METHODS

This investigation was conducted as a soil microcosm leaching study and involved simulated precipitation inputs to undisturbed soil column lysimeters collected from three contrasting forest soils: a Becket series Haplorthod from Old Forge, N.Y., an Unadilla series Dystrochrept from Hanover, N.H., and an Adams series Haplorthod from Ossipee, N.H. These soils were selected to represent a range of contrasting physical-chemical properties with potentially different sensitivities to acidic deposition. In addition, one soil -- the Adirondack Becket -- was chosen to coincide with on-going field investigations by the author and other collaborators on the ILWAS project (The Integrated Lake-Watershed Acidification Study). The comparative environmental, chemical, and physical characteristics of each soil are presented in Tables 1-4.

At each of the three forested sites, ten intact 12cm diameter soil columns were removed from each of three soil depths: 5 cm (O horizon), 20 cm (O+A horizon), and 50 cm (O+A+B horizon). These ninety soil columns were then equipped with plastic tension plates and were installed in a greenhouse at 12-25°C. Over the next 60 weeks, the microcosms were each subjected to a weekly 3.5 cm simulated rain event. Initially, the soil columns were all exposed to a three month baseline period of pH 5.7 simulated rain events. After completion of the pretreatment

TABLE 1

COMPARATIVE ENVIRONMENTAL CHARACTERISTICS OF STUDY SOILS.

PARAMETER	ADAMS	BECKET	UNADILLA
LOCATION	71°8'W,43°47'N	75°0'W,43°40'N	72°17'W,43°42'N
VEGETATION	OAK-PITCH PINE	N. HARDWOOD	WHITE PINE
PARENT MATERIAL	OUTWASH	TILL	LAKE SEDIMENT
SOIL SUBORDER	TYPIC HAPLORTHOD	TYPIC HAPLORTHOD	TYPIC DYSTROCHREPT
SOIL TEXTURE	SAND	SANDY LOAM	SILT/SILT LOAM
% SAND	HIGH	MEDIUM	LOW
% SILT	LOW	MEDIUM	HIGH
PERMEABILITY	HIGH	MEDIUM	LOW
SOIL CHEMISTRY			
pH	INTERMEDIATE	LOW	HIGH
% CaO	LOW	HIGH	INTERMEDIATE
EXCH. Ca	LOW	LOW	HIGH
EXCH. Al	LOW	HIGH	INTERMEDIATE
B.S.I.	INTERMEDIATE	LOW	HIGH

TABLE 2

COMPARATIVE PHYSICAL PROPERTIES OF THE THREE STUDY SOILS. VALUES REPRESENT AVERAGES FOR THE UPPER 50 CM OF SOIL.

SOIL	% SAND 2-0.05 mm	% SILT 0.05-.002 mm	% CLAY <0.002 mm	GRAPHIC MEAN mm	MEDIAN mm	PERMEABILITY cm sec^{-1}
ADAMS	92.6	6.2	1.2	0.43	0.41	5.60×10^{-3}
BECKET	62.2	31.3	6.5	0.21	0.12	2.47×10^{-4}
UNADILLA	14.7	79.2	6.1	0.03	0.023	1.74×10^{-4}

TABLE 3

COMPARATIVE BULK XRF CHEMISTRY FOR THE THREE STUDY SOILS. VALUES ARE MEANS FOR UPPER 80 CM.

SOIL	Fe_2O_3	MnO	TiO_2	CaO	K_2O	P_2O_5	SiO_2	Al_2O_3	MgO	Na_2O	TOTAL
ADAMS	1.06	0.02	0.17	0.47	2.76	0.09	83.99	9.26	0.11	2.00	99.93
BECKET	5.48	0.02	1.01	1.74	3.25	0.12	74.11	11.74	0.94	1.70	100.03
UNADILLA	6.10	0.04	0.98	0.99	2.42	0.23	70.48	15.87	1.13	1.68	99.90

VALUES ARE WT. %

TABLE 4

COMPARISON OF EXCHANGEABLE ELEMENT POOLS

SOIL	MASS MT/ha	Ca	TOTAL BASE CATIONS
		------Eeq/ha	----------
ADAMS			
O	310	6.1	9.0
O+A	2,040	8.0	13.2
O+A+B	5,370	8.4	14.6
BECKET			
O	140	3.8	4.9
O+A	1,330	7.8	10.8
O+A+B	4,000	9.8	14.1
UNADILLA			
O	100	5.5	7.3
O+A	1,530	12.9	18.2
O+A+B	4,760	27.2	40.6

period, the columns were distributed in a stratified random fashion into three treatment groups (pH 5.7, pH 4.0, and pH 3.5) corresponding to the following respective annual H^+ loading rates: 36 eq ha^{-1}, 1,840 eq ha^{-1}, and 5,520 eq ha^{-1}. These weekly treatment storm events continued for eleven months.

During each simulated rain event, soil column leachates were collected under tension in plastic bottles and were then analyzed for pH, AE-pH, Ca, Mg, K, Na, NH_4^+, monomeric Al, SO_4^{2-}, NO_3^-, Cl^-, F^-, and DOC. At the termination of the experiment, the soil columns were dissected into depth increments for analysis and the samples were air-dried. These treatment soil samples and the pretreatment field samples were sieved and the <2mm fraction from each sample was analyzed for exchangeable cations using 1 N NH_4Cl and AAS. Exchangeable acidity was measured by extraction with 1N KCl, followed by titration. Soil horizons from each soil were analyzed for grain size distributions using standard methods of sieving and hydrometer analysis. Each soil horizon (<2mm) was also analyzed for bulk soil chemistry by XRF and for soil mineralogy using x-ray diffraction. Final statistical analyses were performed using the SAS analytical program. Further methodological details are provided elsewhere (1,2).

RESULTS

Weathering Rates

Mass balance data from the soil columns were used to calculate weathering and biological mineralization rates for the three soils and to evaluate how these rates of element replenishment are affected by differences in soil properties and H^+ deposition. For these calculations, the data were plugged into the following equation:

$$\text{Weathering and/or Mineralization} = \text{Leachate Flux} - \text{Input Flux} + \Delta\text{Exchange Pool} + \text{Plant Accumulation}$$

Then, the equation was solved using two alternate boundary assumptions: (1) because there were virtually no statistically significant changes in exchangeable cation pools over the experimental period, the ΔExchange Pool term was set to zero; and

(2) it was assumed that the ΔExchange Pool term could be as large as half the 95% confidence interval on the exchangeable cation measurement. Using this approach, it was possible to produce high and low estimates for each soil column and each separate horizon.

Results from mass balance experiments with the Adams, Becket, and Unadilla soils are summarized in Tables 5-7. These estimates illustrate that cation denudation rates differed significantly between the three contrasting forest soils; thus, the null hypothesis could not be substantiated even for three soils from the same general region of eastern North

TABLE 5

COMPARISON OF CATION DENUDATION RATES (Eq ha^{-1} yr^{-1})

DEPTH	UNADILLA	BECKET	ADAMS
O-HORIZON	3150 (420)	900 (40)	350 (90)
A-HORIZON	4690 (570)	870 (260)	380 (40)
B-HORIZON	3190 (800)	650 (260)	780 (70)
TOTAL A+B	7880	1510	1160
TOTAL O+A+B	11030 (1790)	2410 (550)	1510 (200)

STANDARD ERROR IN PARENTHESIS

BASED UPON AN ANNUAL WATER INPUT OF 120 cm.

America. As shown in Table 5, weathering/mineralization rates between soils varied ten-fold in the A-horizon, ranging from 4,690 eq ha^{-1} yr^{-1} in the Unadilla soil to 380 eq ha^{-1} yr^{-1} in the Adams soil. Normalized rates in the same horizon ranged from 3.3 meq Kg^{-1} yr^{-1} in the Unadilla soil to 0.2 meq Kg^{-1} yr^{-1} in the Adams soil (Table 6). In comparison, B-horizon weathering rates ranged from 3,190 eq ha^{-1} yr^{-1} in the Unadilla

TABLE 6

NORMALIZED AVERAGE WEATHERING/MINERALIZATION RATES EXPRESSED IN Meq kg^{-1} yr^{-1}.

DEPTH	UNADILLA	BECKET	ADAMS
O-HORIZON	31.5	6.4	1.3
	(4.2)	(0.3)	(0.4)
A-HORIZON	3.3	0.7	0.2
	(0.4)	(0.2)	(0.03)
B-HORIZON	1.0	0.2	0.2
	(0.2)	(0.1)	(0.02)

STANDARD ERROR IN PARENTHESIS

TABLE 7

MINIMUM AVERAGE WEATHERING/MINERALIZATION RATES CORRECTED FOR ERRORS IN THE ESTIMATION OF SOIL EXCHANGEABLE CATION CONCENTRATIONS. UNITS: Eq $ha^{-1}yr^{-1}$.

DEPTH	UNADILLA	BECKET	ADAMS
O-HORIZON	170	10	50
A-HORIZON	2410	30	4
B-HORIZON	390	50	540
TOTAL A+B	2800	80	540
TOTAL O+A+B	2970	90	590

profile to less than 800 eq ha^{-1} yr^{-1} in the Becket and Adams soils; similarly, normalized weathering rates varied four-fold between the Unadilla B-horizon at 1.0 meq Kg^{-1} yr^{-1} and the Becket and Adams soils at 0.2 meq Kg^{-1} yr^{-1}. Overall, the analysis presented in Table 5 indicated that total mineral soil profile cation denudation rates ranged seven-fold from 7.9 Keq ha^{-1} yr^{-1} in the fine-textured Unadilla Inceptisol to 1.2 Keq ha^{-1} yr^{-1} in the sandy Adams Spodosol.

Using the alternate mass balance boundary assumption described earlier, it was also possible to estimate minimum weathering/mineralization rates for the three soils (Table 7). Based upon these values, it is apparent that much of the base cation flux from all three soils could potentially be accounted for by statistically undetectable changes in the soil exchangeable element pools. Thus, weathering/mineralization rates could be as low as 2,800 eq ha^{-1} yr^{-1} in the Unadilla mineral soil profile, 80 eq ha^{-1} yr^{-1} in the Becket mineral profile, and 540 eq ha^{-1} yr^{-1} in the Adams profile.

The study also provided an important opportunity to compare weathering estimates obtained by several independent methods. In Table 8, the high and low mass balance estimates for each soil are compared with weathering rates based upon sodium and silica fluxes from each soil. The table also includes two additional estimates for the Becket Spodosol derived from field studies by April and Newton (3) and Likens et al. (4). As such, the data illustrate several significant points. First, the different estimation techniques provided weathering rates that varied by as much as 20X for a given soil. In comparing techniques, the silica flux method tended to yield the lowest weathering rates, the sodium flux method produced intermediate estimates, and the mass balance approach provided the highest weathering rates. Yet, in spite of the great variation in results, there were indications of convergence among some procedures. In the Becket soil, results of mass balance, sodium flux, and watershed input-output budget calculations indicated that the soil profile weathering rate lies between 1.0 - 1.5 Keq ha^{-1} yr^{-1}. In comparison, the minimum mass balance estimate and the sodium flux estimate for the Unadilla soil indicated that the weathering rate for this soil profile lies between 2.6 - 2.8

TABLE 8

COMPARISON OF WEATHERING RATES FOR EACH SOIL BASED UPON SEVERAL DIFFERENT ESTIMATION TECHNIQUES. WEATHERING IS TAKEN TO BE THE SUM OF Ca + Mg + K + Na RELEASED FROM PRIMARY MINERALS IN Eq ha^{-1} yr^{-1}.

METHOD	ADAMS	BECKET	UNADILLA
Mass Balance (Maximum)[a]	1,160	1,510	7,876
Mass Balance (Minimum)[a]	540	80	2,800
Sodium Flux Ratio[b]	320	1,030	2,590
Silica Flux Ratio[c]	60	250	330
Mineral Depletion[d]	--	620	--
Watershed Budget			
ILWAS[e]	--	1,480	--
Hubbard Brook[f]	--	2,000	--

[a] From the soil column mass balance experiments (Tables 5 & 7).

[b] Because sodium is considered to be relatively conservative, the solution Na flux and bulk XRF chemistry were used to calculate the release of Ca + Mg + K necessary to account for the observed Na flux.

[c] This technique makes the tenous assumption that solution silica flux is directly related to the rate of release of Si + Ca + Mg + K + Na from primary minerals.

[d] This estimate from April and Newton (1984) is based on a long-term weathering rate determined from mineral depletion in the Becket soil profile of Woods watershed.

[e] This estimate is based on data from the ILWAS watersheds where the Becket Spodosol was obtained. The estimate combines the annual stream export of cations from Woods Lake watershed (April and Newton 1984) with an estimate of the annual biomass increment of cations (Cronan, unpubl. data).

[f] The Hubbard Brook Experimental Forest in New Hampshire (Likens et al. 1977) contains the same Becket Spodosol as the Adirondack soil used in this study.

Keq ha^{-1} yr^{-1}. Finally, although the Adams soil exhibited less clear-cut convergence, the intermediate sodium flux estimate and minimum mass balance estimate indicate that the weathering rate for this soil probably falls in the range of 0.3-0.6 Keq ha^{-1} yr^{-1}.

With soil depth included in the experimental design, it was possible to examine differential leaching fluxes and element turnover rates through the separate soil horizons. As shown in Table 6, this analysis revealed a number of distinct differences in weathering/mineralization rates between soil horizons. First, the normalized forest floor (O-horizon) rates of base cation mineralization were all 5-10X higher than base cation release rates in the mineral horizons. In addition, the Unadilla and Becket A horizons exhibited unit mass weathering rates that were approximately 3X higher than B-horizon rates of weathering. As such, this confirms and quantifies the pattern of cation denudation that one would expect in the zone of intense weathering beneath the acid forest floor. In fact, if one adds the flux of aqueous aluminum from the A-horizon, the inter-horizon differences in weathering rates would increase to approximately 4-5X. In comparison to the Unadilla and Becket soils, unit base cation weathering rates in the Adams soil were low and nearly identical in the A and B horizons. Again, however, the addition of aqueous aluminum to the A horizon cation flux would boost the overall cation denundation rate in the A horizon above the B horizon rate.

Controls on Weathering: Soil Properties

As might be expected, the three contrasting study soils exhibited distinct differences in mineral weathering rates. These differences were reflected in leachate solution chemistry (Table 9) and in calculated total ion flux estimates (Tables 5-7). Given these differences, one of the prime objectives of this investigation was to exploit the three soils to examine the influence of selected physical, chemical, and biological parameters in controlling the patterns of chemical weathering in acid forest soils.

TABLE 9

EXAMPLES OF TREATMENT PERIOD (pH 3.5 TREATMENT) LEACHATE CHEMISTRY FROM THE O, A, AND B HORIZONS OF EACH STUDY SOIL. ALUMINUM DATA ARE IN ug l^{-1}, WHILE OTHERS ARE IN ueq l^{-1}.

HORIZON	pH	Ca	Mg	K	Na	Al_a	SBC	SO_4^{2-}	NO_3^-	Cl^-	F^-
RAIN INPUT	3.52	20	10	25	5	0	60	330	30	10	0
ADAMS											
O-HORIZON	4.30	39	13	87	13	290	152	428	61	20	1
A-HORIZON	4.55	61	42	161	24	850	288	444	76	34	1
B-HORIZON	5.50	169	47	154	29	0	399	18	368	31	1
BECKET											
O-HORIZON	3.62	85	25	44	8	140	162	435	195	19	1
A-HORIZON	4.01	190	75	71	31	3,870	367	238	1,155	23	4
B-HORIZON	4.15	212	102	64	44	3,870	422	74	1,819	41	10
UNADILLA											
O-HORIZON	3.76	474	118	55	7	810	654	414	450	18	1
A-HORIZON	4.13	1,154	276	85	31	3,690	1,546	161	2,385	23	19
B-HORIZON	4.64	1,520	538	20	122	390	2,200	117	2,280	49	9

SBC= SUM OF BASE CATIONS

The initial focus of this analysis was to examine the differential influence of soil type and varible physical-chemical properties on mineral weathering rates. To begin, the data were used to test the hypothesis that weathering is inversely proportional to soil particle size and increases with increasing surface area. As shown in Fig. 1, the data from the three soils fit a negative decay curve and thus supported the hypothesis that mineral weathering rate in the bulk soil profile is strongly related to grain size. In a related test, the data were used to evaluate the hypothesis that weathering is a rate-limited non-equilibrium process which increases per unit area with decreasing soil permeability and increasing soil water residence time. This auto-correlated test provided essentially the inverse relationship of the previous case, indicating that over a range of soil water

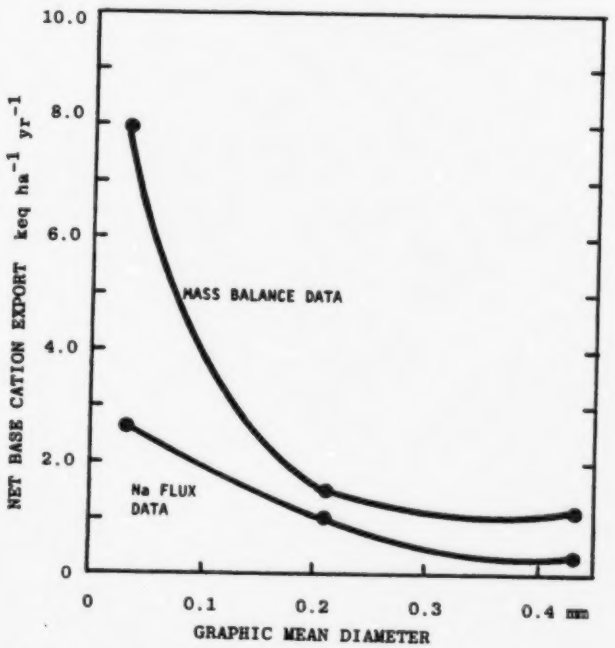


FIG. 1. RELATIONSHIP BETWEEN WEATHERING RATE AND MEAN SOIL PARTICLE SIZE IN EACH STUDY SOIL.

residence times from 2-80 hr., cation export increased with increasing residence time.

Despite close similarities in the mineralogical characteristics of the three soils, an attempt was made to test the hypothesis that weathering rate is controlled by source mineralogy and is proportional to cation concentration in the primary mineral substrate. This hypothesis assumes that simple congruent dissolution of a unit of mineral will yield soluble cation concentrations in proportion to their mineralogical abundance. When the data were examined, the differences in base cation equivalents in the bulk soil proved to be relatively small and were not clearly related to weathering rates. This may indicate: (1) that there are other overriding or intermediate processes (e.g. selective ion exchange) which control solution composition, or (2) that weathering rate is controlled by minor minerals that are poorly represented by an XRF bulk chemistry measurement.

Another concern in this study was to examine the influence of soil chemistry on chemical weathering estimates. One of the critical problems in using the mass balance difference method to calculate weathering is the difficulty in detecting small changes in exchangeable cations. This can introduce a major uncertainty regarding the proportion of cation export attributable to primary weathering versus net depletion of exchangeable cations. In this study, the comparative data were used to explore the relationships between primary weathering, soil exchange chemistry, and net base cation export in the three soil profiles. As shown in Fig. 2, there was a rather smooth exponential increase in cation denudation as one moved from the Adams soil with a total exchangeable base cation reserve of 5.6 keq ha^{-1}, to the Becket soil at 9.2 keq ha^{-1}, and finally to the Unadilla soil with an exchangeable base reservoir of 33.3 keq ha^{-1}. This could be interpreted to indicate that base cation export is controlled in part by the exchangeable base pool and that the observed cation export fluxes may be largely derived from depletion of the soil exchange complex. Yet, if the data in Fig. 2 are used to calculate element turnover times for each soil, it is clear that these observed cation export rates are high enough to deplete the exchangeable bases in each soil within 4-6 yrs (or 8-12 yrs. if

the water flux estimate is halved to a more conservative level).

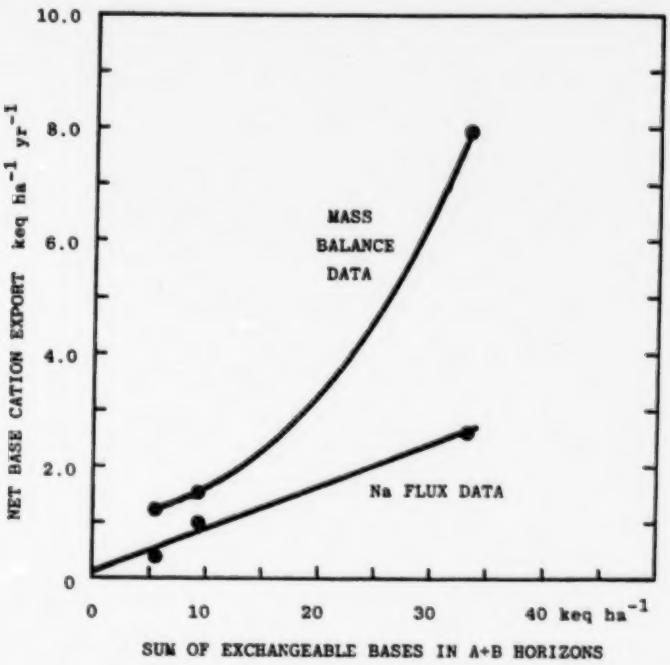


FIG. 2. RELATIONSHIP BETWEEN WEATHERING RATE AND TOTAL EXCHANGEABLE BASES IN EACH SOIL.

Since this depletion obviously could not be sustained and because all other evidence indicates a relatively stable exchange pool, it can be concluded that (1) the exchange pool acts as the immediate response reservoir and as a modifier of solution ionic chemistry; and (2) while high rates of cation export draw upon exchangeable base supplies as a proximal source, sustained cation export is ultimately possible because the base cation weathering rate balances the rate of exchangeable base depletion through leaching. Thus, base cation exports correlate with soil exchangeable base supply because both are dependent on the same master variable, the base cation weathering rate.

Controls on Weathering: Biotic Processes

There are a number of plant-mediated and microbial processes which may affect weathering in forest soils, including: forest canopy enhancement of dry deposition of acidic and acid-forming substances; soil acidification resulting from plant nutrient uptake; biological respiration; biological production and release of organic acids; and microbial nitrification. In this study, it was possible to examine the influence of two of these factors - organic acid generation and nitrification - on mineral weathering patterns in the three soils.

One of the study hypotheses was that weathering increases as a function of increasing organic acidity and organic complexation. As shown in Fig. 3, DOC concentrations in forest floor leachates were substantial in all three soils and ranged three-fold from 19 mg l^{-1} C in the Becket O-horizon to 64 mg l^{-1} C in the Adams O-horizon.

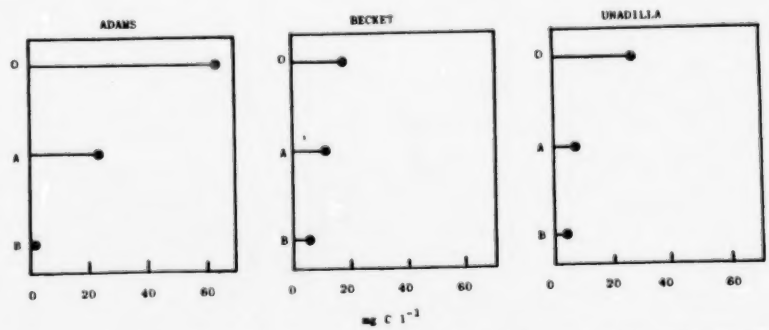


FIG. 3. COMPARATIVE LEACHATE DOC CONCENTRATIONS IN THE O, A, AND B HORIZONS OF THE THREE STUDY SOILS

Previous studies with the same soils (5) have shown that much of this DOC is comprised of acidic humic substances characterized by an average carboxyl group content of ca. 6 meq gm^{-1} C, with an average pK_a of approximately 3.8 (Table 10). If one extrapolates with these figures to an annual flux estimate, one can calculate that each Kg of soil in the uppermost A-horizon of each soil is exposed to

0.2 - 2.0± meq of organic acid derived protons each year. Furthermore, these organic acids may exert a strong influence on weathering reactions through metal complexation. Comparing just the proton input from the organic acids with the normalized weathering rates in Table 6, one can see that biologically-derived organic acidity and complexation can make a significant, if not dominant, contribution to weathering in the upper soil zone. Thus, within a given soil, it is likely that increases in organic acid release would produce increased weathering. However, in comparing different soils, it appears that fluxes of organic acidity are secondary to other factors in controlling weathering.

Nitrification, like plant uptake, can act as a net acidifying process in soils. As such, it can potentially contribute to accelerated cation export from the soil. In most systems with intact plant communities, there appears to be little direct net contribution from nitrification to the proton budget of the soil. However, where plant uptake is interrupted or where a forest reaches nitrogen saturation (6), nitrification potential may be expressed as a strong pulse of acidity. In this study, nitrification was pronounced in the soil columns and this permitted an examination of the influence of internal acid generation by nitrification upon cation export rates of different soils. This analysis showed that differences in cation export fluxes between the three soils were not clearly related to differences in nitrification and the resulting nitrate flux. In fact, the Becket and Unadilla soils shared the same nitrate flux, but differed 2-5X in cation export. Hence, inter-soil differences in weathering rate seemed to be dominated by other factors than internal acidification by nitrification.

TABLE 10
FUNCTIONAL GROUP ANALYSIS AND ESTIMATION OF AVERAGE pK_a
FOR O/A HORIZON SOIL SOLUTIONS COLLECTED DURING THE SUMMER

pH	3.55
H^+	284 μeq/l
Acidity to pH 7	510 μeq/l
Acidity to pH 9	635 μeq/l
Al_a (Monomeric aluminum)	51 μeq/l
Ratio of Al_o/Al_a	0.79
Fe	9 μeq/l
DOC	52 mg/l
COOH	166 μeq/l
Total COO^- (Anion Deficit)	134 μeq/l
Metal Bound COO^-	49 μeq/l
Free COO^-	85 μeq/l
Total Carboxyl Group Content	5.77 meq g^{-1} C
Estimated Average pK_a	3.84

Controls on Weathering: H^+ Deposition

One of the final objectives of this investigation was to test the effects of strong acid deposition upon weathering rates within contrasting forest soils. This question was of interest because of concern that acidic deposition may deplete soils of available bases faster than they are replenished by weathering. The experiment also offered an important opportunity to examine general patterns of weathering response to increased H^+ inputs. In Fig. 4, weathering rates have been plotted for each soil as a function of the three treatment H^+ deposition rates. To account for baseline differences between soil columns, the soil columns were compared statistically using net mean differences in element fluxes between treatment and pretreatment periods.

These net changes in cation denudation are plotted on the graph and indicate that the Adams and Unadilla soils both exhibited significantly increased base cation exports in response to increased H^+ deposition. In contrast, the Becket soil provided a pattern that was not directly related to H^+ inputs and which may have been dominated by inter-column differences in nitrification, sulfate adsorption, labile aluminum, or the like.

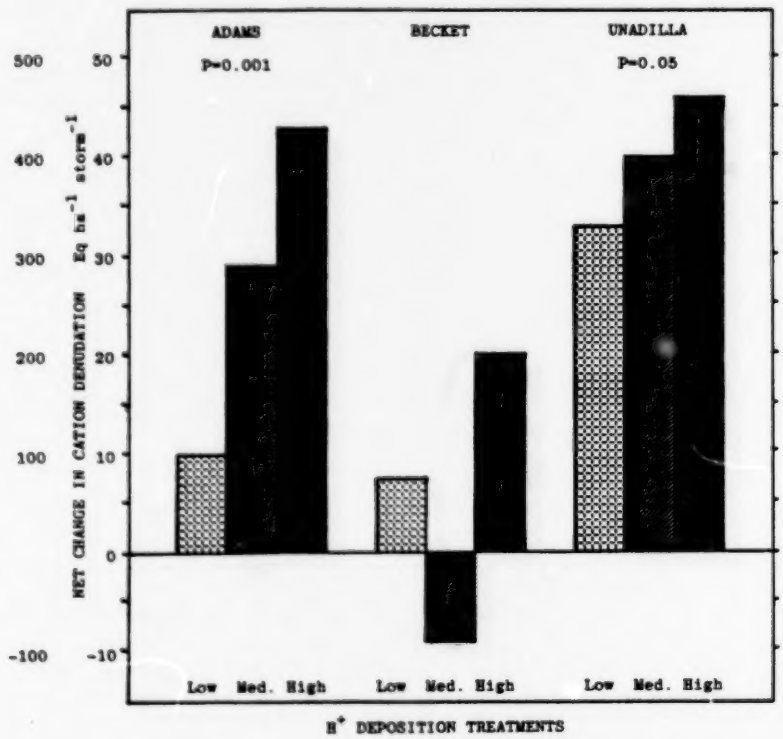


FIG. 4. COMPARISON OF TREATMENT H^+ DEPOSITION EFFECTS ON RATES OF CATION EXPORT FROM EACH SOIL. LOW, MEDIUM, AND HIGH TREATMENTS REFER TO 1, 35, and 106 Eq ha^{-1} $storm^{-1}$, RESPECTIVELY. TO NORMALIZE EACH TREATMENT GROUP, SOIL COLUMNS WERE COMPARED STATISTICALLY USING NET MEAN DIFFERENCES IN ELEMENT FLUXES BETWEEN TREATMENT AND TREATMENT PERIODS. THE LOWER RANGE ON THE Y-AXIS APPLIES TO THE ADAMS AND BECKET SOILS.

SUMMARY

In this investigation, weathering rates were estimated for three eastern North American forest soils and leaching experiments were performed to examine the influence of selected environmental variables on the weathering process. Based upon multiple estimation techniques, mineral soil weathering rates varied five-fold between soils, ranging from approximately 0.5 Keq ha^{-1} yr^{-1} in the sandy Adams Spodosol, to 1.2 Keq ha^{-1} yr^{-1} in the sandy loam Becket Spodosol, to 2.7 Keq ha^{-1} yr^{-1} in the silty Unadilla Inceptisol. Inter-soil differences in weathering rate were inversely correlated with mean soil particle size and positively correlated with total exchangeable bases in the soil profile. The fact that cation export correlated with exchangeable bases has been interpreted not to be a direct causal relationship. Instead, the pattern illustrates that as the weathering rate increases, both cation export and exchangeable base replenishment increase (i.e. both high exchangeable base status and high rates of base cation export are indicative of a sustained high rate of weathering). Study results also demonstrated major differences in weathering rates between soil horizons. A-horizons from the Unadilla Inceptisol and Becket Spodosol exhibited unit mass weathering rates for base cations that were three-fold higher than B horizon rates of weathering. Finally, study results also indicated that soil column cation denudation increased in the Adams Spodosol and Unadilla Inceptisol as treatment inputs of acid deposition increased from .04 Keq ha^{-1} yr^{-1} to 1.8 Keq ha^{-1} yr^{-1} to 5.5 Keq ha^{-1} yr^{-1}.

REFERENCES

(1) Cronan, C.S. 1984. Comparative effects of precipitation acidity on three forest soils: impacts on nutrient availability. In review.

(2) Cronan, C.S. 1984. Comparative effects of precipitation acidity on three forest soils: carbon cycling responses. Plant and Soil :submitted.

(3) April, R. and Newton, R.M. 1984. Geology and geochemistry of the ILWAS watersheds. Water, Air, Soil Pollut. :submitted.

(4) Likens, G.E., F.H. Bormann, R.S. Pierce, J.S. Eaton, and N.M. Johnson. 1977. Biogeochemistry of a Forested Ecosystem. Springer-Verlag. N.Y. 146 p.
(5) Cronan, C.S.and G.R. Aiken. 1984. Chemistry and movement of dissolved humic substances in ILWAS watersheds, Adirondack Park, N.Y. In review.
(6) Ulrich, B. 1983. Stabilität von waldökosystemen unter dem einfluß des sauren regen. Allgemeine Forst Zeitschrift 26/27 pp. 670-677.
(7) Johnson, N.M., C.T. Driscoll, J.S. Eaton, G.E. Likens, and W.H. McDowell. 1981. Acid rain, dissolved aluminum, and chemical weathering at the Hubbard Brook Experimental Forest, New Hampshire. Geochim. Cosmochim. Acta 45, pp. 1421-1437.